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A NEW ANALYSIS OF MOLECULAR DIMENSIONS

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A NEW ANALYSIS OF MOLECULE DIMENSIONS

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ABSTRACT: It is shown that the size of the molecules of a
substance dissolved in an undissociated dilute solution can
be determined from the internal friction of the solution in
in the solvent and diffusion of the dissolved substance in
the solvent, providing the molecular volume of the dissolved
substance is greater than that of the solvent. This is
done by applying hydrodynamic equations to the solvent,
considering the liquid is homogeneous and therefore without
molecular structure.

The oldest determination of the true magnitude of the molecule was made   /289*
possible by the kinetic theory of gases, while physical phenomena observed in
liquids have not yet been of service in determining molecule sizes.

This is undoubtedly based on the difficulties, insuperable up to now, which
oppose the development of a detailed molecular-kinetic theory of liquids. In
this work it will now be shown that the magnitude of the molecules of the
material dissolved in an undissociated dilute solution can be determined from
the internal friction of the solution in the pure solvent and from the diffusion
of the dissolved material in the solvent, if the volume of one molecule of the
dissolved material is larger than the volume of a molecule of the solvent. This
is because a dissolved molecule of this type will behave approximately like a
solid body suspended in the solvent in regard to its mobility in the solvent
and in regard to its influence on the internal friction of the solvent, and it
will be possible to apply to the movement of the solvent immediately next to a
molecule the hydrodynamic equations in which the liquid is considered as
homogeneous, therefore not considered as having a molecular structure. For the
shape of the solid bodies, which are to represent the dissolved molecules, let
us choose spheres.

§ 1. The Influence of a Very Small Sphere Suspended in a Liquid Upon the
Movement of that Liquid.

Let an incomprehensible homogeneous liquid with coefficient of friction k
lie at the basis of this consideration with velocity components u, v, w
given as functions of the coordinates x, y, z and time. Beginning at any point
x_0, y_0, z_0, let us imagine the functions u, v, w as functions of $x - x_0$, $y - y_0$,
$z - z_0$ developed according to the Taylor series; and such a small area G be   /290

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limited around this point that within it only the linear members of this develop-
ment can be considered. The movement of the fluid contained in G can then, as
is known, be understood as the superposition of three movements, viz.

1. a parallel displacement of all fluid particles without any alteration
in their relative position,

2. circulation of the liquid without alteration in the relative position
of the fluid particles,

3. an expansion movement in three directions perpendicular to each other
(the main expansion direction).

Now let us imagine in area G a rigid, spherical body, the midpoint of
which lies at point x_0, y_0, z_0 and the dimensions of which are much smaller than
that of area G. Let us further assume that the movement under consideration is
so slow that the kinetic energy of the sphere, as well as that of the liquid,
can be disregarded. Let it further be assumed that the velocity components of
a surface element of the sphere correspond with the corresponding velocity
components of the adjacent fluid particles, i.e. that the separation layer
(thought of as continuous) exhibits a finitely small coefficient of internal
friction everywhere.

It is immediately clear that the sphere participates simply in partial
movements 1. and 2., without modifying the movement of the adjacent fluid, since
the fluid behaves as a rigid body in these partial movements and since we over-
look the effects of inertia.

However, movement 3. is modified by the presence of the sphere and our
next task will be to investigate the influence of the sphere on this fluid
movement. If we equate movement 3. to a coordinate system with axes parallel
to the main expansion directions, and if we posit

$$x - x_0 = \xi,$$
$$y - y_0 = \eta,$$
$$z - z_0 = \zeta,$$

that movement, if the sphere is not present, can be represented by the equations:/291

$$\begin{cases} u_0 = A\,\xi, \\ v_0 = B\,\eta, \\ w_0 = C\,\zeta; \end{cases} \tag{1}$$

A, B, C are constants which, because of the imcompressibility of the liquid,
fulfill the condition:

$$A + B + C = 0. \tag{2}$$

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If the rigid sphere with radius P now finds itself at point x_0, y_0, z_0, the fluid movement is altered in its affinity. For the sake of convenience we shall denote below P as "finite", but the values of ξ, η, ζ, for which the fluid movement is no longer modified by the sphere, as "infinitely large".

Because of the symmetry of the fluid movement under consideration, it is then clear that the sphere is incapable of producing either a transference or a turn in the movement under consideration, as we obtain the boundary conditions:

$$u = v = w = 0 \quad \text{for} \quad \varrho = P,$$

in which

$$\varrho = \sqrt{\xi^2 + \eta^2 + \zeta^2} > 0$$

is posited. Here u, v, w signify the velocity components of the movement now considered (modified by the sphere). If we posit

$$\begin{cases} u = A\,\xi + u_1, \\ v = B\,\eta + v_1, \\ w = C\,\zeta + w_1, \end{cases} \tag{3}$$

the velocities u_1, v_1, w_1 would have to disappear into infinity, since the movement presented in equations (3) is to be converted in infinity into the movement presented in equations (1).

The functions u, v, w must satisfy the equations of hydrodynamics with consideration of internal friction and disregard for inertia. Thus the follow- /292 ing equations are valid [1]

$$\begin{cases} \dfrac{\partial p}{\partial \xi} = k\,\Delta u \quad \dfrac{\partial p}{\partial \eta} = k\,\Delta v \quad \dfrac{\partial p}{\partial \zeta} = k\,\Delta w, \\ \dfrac{\partial u}{\partial \xi} + \dfrac{\partial v}{\partial \eta} + \dfrac{\partial w}{\partial \zeta} = 0, \end{cases} \tag{4}$$

in which Δ signifies the operator

$$\frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2} + \frac{\partial^2}{\partial \zeta^2}$$

and p the hydrostatic pressure.

Since equations (1) are solutions of equations (4) and since the latter are linear, the magnitudes u_1, v_1, w_1 must also satisfy equations (4) according to (3). I determined u_1, v_1, w_1 and p according to a method given in § 4 of

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Kirchhoff's lecture mentioned above[1] and found:

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$$\begin{cases} p = -\tfrac{5}{3}\,k\,P^3\left\{ A\,\dfrac{\partial^2\left(\tfrac{1}{\varrho}\right)}{\partial\,\xi^2} + B\,\dfrac{\partial^2\left(\tfrac{1}{\varrho}\right)}{\partial\,\eta^2} + C\,\dfrac{\partial^2\left(\tfrac{1}{\varrho}\right)}{\partial\,\zeta^2}\right\} + \text{const.}, \\[2mm] u = A\,\xi - \tfrac{5}{3}\,P^3\,A\,\dfrac{\xi}{\varrho^3} - \dfrac{\partial\,D}{\partial\,\xi}, \\[2mm] v = B\,\eta - \tfrac{5}{3}\,P^3\,B\,\dfrac{\eta}{\varrho^3} - \dfrac{\partial\,D}{\partial\,\eta}, \\[2mm] w = C\,\zeta - \tfrac{5}{3}\,P^3\,C\,\dfrac{\zeta}{\varrho^3} - \dfrac{\partial\,D}{\partial\,\zeta}, \end{cases} \qquad (5)$$

in which

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[1] "From equations (4) it follows that $\Delta p = 0$. If p is presumed in accord with this condition and if a function V is determined which satisfies the equation

$$\Delta V = \frac{1}{k}\,p$$

equations (4) are fulfilled if we posit

$$u = \frac{\partial V}{\partial\,\xi} + u', \quad v = \frac{\partial V}{\partial\,\eta} + v', \quad w = \frac{\partial V}{\partial\,\zeta} + w'$$

and choose u', v', w' so that $\Delta u' = 0$, $\Delta v' = 0$ and $\Delta w' = 0$ and

$$\frac{\partial\,u'}{\partial\,\xi} + \frac{\partial\,v'}{\partial\,\eta} + \frac{\partial\,w'}{\partial\,\zeta} = -\frac{1}{k}\,p \quad.$$

If we now posit

$$\frac{p}{k} = 2\,c\,\frac{\partial^2\,\tfrac{1}{\varrho}}{\partial\,\xi^2}$$

and in harmony with this

$$V = c\,\frac{\partial^2\,\varrho}{\partial\,\xi^2} + b\,\frac{\partial^2\,\tfrac{1}{\varrho}}{\partial\,\xi^2} + \frac{a}{2}\left(\xi^2 - \frac{\eta^2}{2} - \frac{\zeta^2}{2}\right)$$

and

$$u' = -2\,c\,\frac{\partial\,\tfrac{1}{\varrho}}{\partial\,\xi}, \quad v' = 0, \quad w' = 0,$$

constants a, b, c can be so set that for $\rho = P$, $u = v = w = 0$. By superposing three solutions of this type, the solution given in equations (5) and (5a) are obtained.

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$$\left\{ \begin{aligned} D &= A\left\{\tfrac{5}{6}P^3\frac{\partial^2\varrho}{\partial\xi^2} + \tfrac{1}{6}P^5\frac{\partial^2\left(\frac{1}{\varrho}\right)}{\partial\xi^2}\right\} \\ &+ B\left\{\tfrac{5}{6}P^3\frac{\partial^2\varrho}{\partial\eta^2} + \tfrac{1}{6}P^5\frac{\partial^2\left(\frac{1}{\varrho}\right)}{\partial\eta^2}\right\} \\ &+ C\left\{\tfrac{5}{6}P^3\frac{\partial^2\varrho}{\partial\zeta^2} + \tfrac{1}{6}P^5\frac{\partial^2\left(\frac{1}{\varrho}\right)}{\partial\zeta^2}\right\}. \end{aligned} \right. \tag{5a}$$

It is easy to prove that equations (5) are solutions of equations (4). Then since

$$\Delta\xi = 0, \quad \Delta\frac{1}{\varrho} = 0, \quad \Delta\varrho = \frac{2}{\varrho}$$

and

$$\Delta\left(\frac{\xi}{\varrho^3}\right) = -\frac{\partial}{\partial\xi}\left\{\Delta\left(\frac{1}{\varrho}\right)\right\} = 0,$$

we get

$$k\Delta u = -k\frac{\partial}{\partial\xi}\{\Delta D\} = -k\frac{\partial}{\partial\xi}\left\{\tfrac{5}{3}P^3 A\frac{\partial^2\frac{1}{\varrho}}{\partial\xi^2} + \tfrac{5}{3}P^3 B\frac{\partial^2\frac{1}{\varrho}}{\partial\eta^2} + \ldots\right\}.$$

However, the expression obtained last is identical with $\partial\varrho/\partial\xi$ according to the first of equations (5). In the same way it is shown that the second and third of equations (4) are fulfilled. In addition we get

$$\frac{\partial u}{\partial\xi} + \frac{\partial v}{\partial\eta} + \frac{\partial w}{\partial\zeta} = (A + B + C)$$
$$+ \tfrac{5}{3}P^3\left\{A\frac{\partial^2\left(\frac{1}{\varrho}\right)}{\partial\xi^2} + B\frac{\partial^2\left(\frac{1}{\varrho}\right)}{\partial\eta^2} + C\frac{\partial^2\left(\frac{1}{\varrho}\right)}{\partial\zeta^2}\right\} - \Delta D.$$

However, since according to equation (5a) /294

$$\Delta D = \tfrac{5}{3}AP^3\left\{A\frac{\partial^2\left(\frac{1}{\varrho}\right)}{\partial\xi^2} + B\frac{\partial^2\left(\frac{1}{\varrho}\right)}{\partial\eta^2} + C\frac{\partial^2\left(\frac{1}{\varrho}\right)}{\partial\zeta^2}\right\};$$

it follows that the last of equations (4) is also fulfilled. As far as the boundary conditions are concerned, our equations for u, v, w are then converted into equations (1) for infinitely large ρ. By introducing the value of D from equation (5a) into the second of equations (5), we get:

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$$\begin{cases} u = A\xi - \tfrac{5}{2}\frac{P^3}{\varrho^5}\xi(A\xi^2 + B\eta^2 + C\zeta^2) \\ \quad + \tfrac{5}{2}\frac{P^5}{\varrho^7}\xi(A\xi^2 + B\eta^2 + C\zeta^2) - \frac{P^5}{\varrho^5}A\xi. \end{cases} \tag{6}$$

It is recognized that u disappears for $\rho = P$. The same is valid for v and w for reasons of symmetry. Now it should be demonstrated that satisfaction is provided for both equations (4) and the boundary conditions of the problem by equations (5).

It can also be proven that equations (5) are the only solution of equations (4) compatible with the boundary conditions of the problem. Here the proof is only to be indicated. In finite space the velocity components u, v, w of a liquid may satisfy equations (4). If there still exists another solution of U, V, W of equations (4), in which $U = u$, $V = v$, $W = w$ at the boundaries of the space considered, then $(U - u,\ V - v,\ W - w)$ is a solution of equation (4), in which the velocity components disappear at the boundary of the space. Thus no mechanical work is supplied to the fluid found in the space under consideration. Since we have disregarded the momentum of the liquid, it follows that the work changed into heat in the space under consideration is also equal to zero. From this it is deduced that in the entire space $u = u_1$, $v = v_1$, $w = w_1$ obligatorily, in case the space is at least partially bounded by contiguous walls. By going beyond the bounds this result can also be extended to the case where the space under consideration is infinite, as in the above considered case. It can also be verified that the solution found above is the only solution of the problem.

Now we lay out a sphere of radius R around point x_0, y_0, z_0 where R is infinitely large in contrast to P, and we compute the energy which is transformed into heat in the fluid found inside the sphere (in a unit of time). This energy W is equal to that of the work mechanically supplied to the liquid. If we designate the components of the pressure exerted on the surface of the sphere of radius R with X_n, Y_n, Z_n, then:

$$W = \int (X_n u + Y_n v + Z_n w)\,ds,$$

in which the integral is to be extended over the surface of the sphere of radius R. Here:

$$X_n = -\left(X_\xi \frac{\xi}{\varrho} + X_\eta \frac{\eta}{\varrho} + X_\zeta \frac{\zeta}{\varrho}\right),$$
$$Y_n = -\left(Y_\xi \frac{\xi}{\varrho} + Y_\eta \frac{\eta}{\varrho} + Y_\zeta \frac{\zeta}{\varrho}\right),$$
$$Z_n = -\left(Z_\xi \frac{\xi}{\varrho} + Z_\eta \frac{\eta}{\varrho} + Z_\zeta \frac{\zeta}{\varrho}\right),$$

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in which

$$X_\xi = p - 2k\frac{\partial u}{\partial \xi}, \qquad Y_\zeta = Z_\eta = -k\left(\frac{\partial v}{\partial \zeta} + \frac{\partial w}{\partial \eta}\right),$$

$$Y_\eta = p - 2k\frac{\partial v}{\partial \eta}, \qquad Z_\xi = X_\zeta = -k\left(\frac{\partial w}{\partial \xi} + \frac{\partial u}{\partial \zeta}\right),$$

$$Z_\zeta = p - 2k\frac{\partial w}{\partial \zeta}, \qquad X_\eta = Y_\xi = -k\left(\frac{\partial u}{\partial \eta} + \frac{\partial v}{\partial \xi}\right).$$

The expressions for u, v, w are simplified if we observe that for $\rho = R$ the members with the factor P^5/ρ^5 disappear in contrast to those with the factor P^3/ρ^3. We must posit:

$$\begin{cases} u = A\xi - \frac{5}{2}P^3\dfrac{\xi(A\xi^2 + B\eta^2 + C\zeta^2)}{\varrho^5}, \\[2mm] v = B\eta - \frac{5}{2}P^3\dfrac{\eta(A\xi^2 + B\eta^2 + C\zeta^2)}{\varrho^5}, \\[2mm] w = C\zeta - \frac{5}{2}P^3\dfrac{\zeta(A\xi^2 + B\eta^2 + C\zeta^2)}{\varrho^5}. \end{cases} \qquad (6a)$$

From the first of equations (5), by corresponding omissions, we get for p

$$p = -5kP^3\frac{A\xi^2 + B\eta^2 + C\zeta^2}{\varrho^6} + \text{const.}$$

Then we get:

$$X_\xi = -2kA + 10kP^3\frac{A\xi^2}{\varrho^5} - 25kP^3\frac{\xi^2(A\xi^2 + B\eta^2 + C\zeta^2)}{\varrho^7},$$

$$X_\eta = \qquad + 10kP^3\frac{A\xi\eta}{\varrho^5} - 25kP^3\frac{\eta^2(A\xi^2 + B\eta^2 + C\zeta^2)}{\varrho^7},$$

$$X_\zeta = \qquad + 10kP^3\frac{A\xi\zeta}{\varrho^5} - 25kP^3\frac{\zeta^2(A\xi^2 + B\eta^2 + C\zeta^2)}{\varrho^7},$$

and from here

$$X_n = 2Ak\frac{\xi}{\varrho} - 10AkP^3\frac{\xi}{\varrho^4} + 25kP^3\frac{\xi(A\xi^2 + B\eta^2 + C\zeta^2)}{\varrho^6}.$$

With the aid of the expressions for Y_n and Z_n, to be derived by cyclic substitution, along with the omission of all members which contain the ratio P/ρ in a power higher than the third, we get:

$$X_n u + Y_n v + Z_n w + \frac{2k}{\varrho}(A^2\xi^2 + B^2\eta^2 + C^2\zeta^2)$$

$$- 10k\frac{P^3}{\varrho^4}(A^2\xi^2 + . + .) + 20k\frac{P^3}{\varrho^6}(A\xi^2 + . + .)^2.$$

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If we integrate over the sphere and consider that

$$\int ds = 4\,R^2\,\pi,$$

$$\int \xi^2\,ds = \int \eta^2\,ds = \int \zeta^2\,ds = \tfrac{4}{3}\,\pi\,R^4,$$

$$\int \xi^4\,ds = \int \eta^4\,ds = \int \zeta^4\,ds = \tfrac{4}{5}\,\pi\,R^6,$$

$$\int \eta^2\,\zeta^2\,ds = \int \zeta^2\,\xi^2\,ds = \int \xi^2\,\eta^2\,ds = \tfrac{4}{15}\,\pi\,R^6,$$

$$\int (A\,\xi^2 + B\,\eta^2 + C\,\zeta^2)^2\,ds = \tfrac{4}{15}\,\pi\,R^6\,(A^2 + B^2 + C^2),$$

we obtain:

$$W = \tfrac{8}{3}\,\pi\,R^3\,k\,\delta^2 - \tfrac{3}{3}\,\pi\,P^3\,k\,\delta^2 = 2\,\delta^2\,k\,(V - \Phi),\qquad\qquad (7)$$

in which

$$\delta = A^2 + B^2 + C^2,$$

$$\tfrac{4}{3}\,\pi\,R^3 = V$$

and

$$\tfrac{4}{3}\,\pi\,P^3 = \Phi$$

are posited. If the suspended sphere were not present ($\Phi = 0$), we would have obtained for the energy consumed in the volume V

$$W_0 = 2\,\delta^2\,k\,V. \qquad\qquad (7a)$$

Thus the presence of the sphere diminishes the energy consumed by $2\delta^2 k\Phi$. It is /297 worth noting that the influence of the suspended sphere on the magnitude of the energy consumed is just as large as it would have been if the movement of the fluid surrounding the sphere were not at all modified by its presence.

§ 2. Computation of the Coefficient of Friction of a Fluid in which Very Many
    Small Spheres are Suspended in Irregular Distribution.

We have just considered the case where a sphere, relatively very small, is suspended in an area G of the above defined order of magnitude and have investigated how the sphere influences the fluid movement. We shall now assume that infinitely many spheres are irregularly distributed in the area G with identical radii so small that the volume of all the spheres together is very small in contrast to the area G. Let the number of spheres occurring in this unit of

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volume be n, in which n is constant as far as it matters every place in the fluid.

We shall now proceed further from the movement of a homogeneous liquid without suspended spheres and again consider the most general expansion movement. If small spheres are present, a suitable choice will enable us to represent the velocity components u_0, v_0, w_0 at any point x, y, z of area G by the equations:

$$u_0 = A x,$$
$$v_0 = B y,$$
$$w_0 = C z,$$

in which

$$A + B + C = 0.$$

A sphere suspended at point x_ν, y_ν, z_ν now influences the movement in a way visible from equation (6). Since we select the mean distance between adjacent spheres as much larger than their radii, and since consequently the admissible velocity components of all suspended spheres touching each other are small when compared to u_0, v_0, w_0, for the velocity components u, v, w of the spheres suspended in the fluid under consideration and with omission of the members of higher orders, we get: /298

$$
\left\{
\begin{aligned}
u &= A x - \sum \left\{ \frac{5}{2} \frac{P^3}{\varrho_\nu^2} \frac{\xi_\nu (A \xi_\nu^2 + B \eta_\nu^2 + C \zeta_\nu^2)}{\varrho_\nu^3} \right. \\
&\qquad \left. - \frac{5}{2} \frac{P^5}{\varrho_\nu^4} \frac{\xi_\nu (A \xi_\nu^2 + B \eta_\nu^2 + C \zeta_\nu^2)}{\varrho_\nu^3} + \frac{P^5}{\varrho_\nu^4} \frac{A \xi_\nu}{\varrho_\nu} \right\}, \\[2mm]
v &= B y - \sum \left\{ \frac{5}{2} \frac{P^3}{\varrho_\nu^2} \frac{\eta_\nu (A \xi_\nu^2 + B \eta_\nu^2 + C \zeta_\nu^2)}{\varrho_\nu^3} \right. \\
&\qquad \left. - \frac{5}{2} \frac{P^5}{\varrho_\nu^4} \frac{\eta_\nu (A \xi_\nu^2 + B \eta_\nu^2 + C \zeta_\nu^2)}{\varrho_\nu^3} + \frac{P^5}{\varrho_\nu^4} \frac{B \eta_\nu}{\varrho_\nu} \right\}, \\[2mm]
w &= C z - \sum \left\{ \frac{5}{2} \frac{P^3}{\varrho_\nu^2} \frac{\zeta_\nu (A \xi_\nu^2 + B \eta_\nu^2 + C \zeta_\nu^2)}{\varrho_\nu^3} \right. \\
&\qquad \left. - \frac{5}{2} \frac{P^5}{\varrho_\nu^4} \frac{\zeta_\nu (A \xi_\nu^2 + B \eta_\nu^2 + C \zeta_\nu^2)}{\varrho_\nu^3} + \frac{P^5}{\varrho_\nu^4} \frac{C \zeta_\nu}{\varrho_\nu} \right\},
\end{aligned}
\right.
\tag{8}
$$

in which summation is to be extended over all spheres of area G and

$$\xi_\nu = x - x_\nu,$$
$$\eta_\nu = y - y_\nu, \quad \varrho_\nu = \sqrt{\xi_\nu^2 + \eta_\nu^2 + \zeta_\nu^2},$$
$$\zeta_\nu = z - z_\nu$$

are to be posited. x_ν, y_ν, z_ν are the coordinates of the midpoints of the spheres. We further determine from equations (7) and (7a) that the presence of each of the cubes up to an infinitely small higher order has as a consequence a reduction in heat production per unit of time of $2\delta^2 k\Phi$, and that the energy converted into heat in the area G per unit of volume has the value:

$$W = 2\,\delta^2\,k - 2\,n\,\delta^2\,k\,\Phi,$$

or

$$W = 2\,\delta^2\,k\,(1 - \varphi), \tag{7b}$$

where ϕ signifies the fraction of the volume taken up by the spheres.   /299

Equation (7b) produces the likelihood that the coefficient of friction of the heterogeneous mixture of fluid and suspended spheres considered by us (hereafter "mixture" for short) is smaller than the coefficient of friction k of the fluid. However, this is not the case, since A, B, C are not the values of the main expansions of the fluid movement presented in equations (8); we shall name the main expansions of the mixture A^x, B^x, C^x. From reasons of symmetry it follows that the main expansion directions of the mixture are parallel to the directions of the main expansions A, B, C, thus to the coordinate directions. Let us write equations (8) in the form:

$$u = A\,x + \sum u_\nu,$$
$$v = B\,y + \sum v_\nu,$$
$$w = C\,z + \sum w_\nu,$$

and we get:

$$A^x = \left(\frac{\partial u}{\partial x}\right)_{x=0} = A + \sum\left(\frac{\partial u_\nu}{\partial x}\right)_{x=0} = A - \sum\left(\frac{\partial u_\nu}{\partial x_0}\right)_{x=0}.$$

If we exclude the immediate surroundings of the individual spheres from consideration, we can omit the second and third members of the expressions of u, v, w and for $x = y = z = 0$ get:

$$
\begin{cases}
u_\nu = -\frac{5}{2}\frac{P^3}{r_\nu^2}\frac{x_\nu(A\,x_\nu^2 + B\,y_\nu^2 + C\,z_\nu^2)}{r_\nu^3}, \\[2ex]
v_\nu = -\frac{5}{2}\frac{P^3}{r_\nu^2}\frac{y_\nu(A\,x_\nu^2 + B\,y_\nu^2 + C\,z_\nu^2)}{r_\nu^3}, \\[2ex]
w_\nu = -\frac{5}{2}\frac{P^3}{r_\nu^2}\frac{z_\nu(A\,x_\nu^2 + B\,y_\nu^2 + C\,z_\nu^2)}{r_\nu^3},
\end{cases}
\tag{9}
$$

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where

$$r_\nu = \sqrt{x_\nu^2 + y_\nu^2 + z_\nu^2} > 0$$

is posited. Let us extend the summation over the volume of a sphere K of very large radius R of which the midpoint lies in the origin of coordinates. If we further consider the *irregularly* distributed spheres as *uniformly* distributed /300 and replace the sum with an integral, we get:

$$A^* = A - n \int_K \frac{\partial u_\nu}{\partial x_\nu} \, dx_\nu \, dy_\nu \, dz_\nu .$$

$$= A - n \int \frac{u_\nu x_\nu}{r_\nu} \, ds ,$$

where the last integral is to be extended over the surface of the sphere K. Considering (9) we find:

$$A^* = A - \tfrac{5}{2} \frac{P^3}{R^3} n \int x_0^2 (A x_0^2 + B y_0^2 + C z_0^2) \, ds ,$$

$$= A - n \left(\tfrac{4}{3} P^3 \pi\right) A = A (1 - \varphi) .$$

Is- analagously

$$B^* = B (1 - \varphi),$$

$$C^* = C (1 - \varphi).$$

If we posit

$$\delta^* = A^{*2} + B^{*2} + C^{*2},$$

then up to an infinitely small higher order:

$$\delta^{*2} = \delta^2 (1 - 2 \varphi).$$

For heat development per unit of time and volume we have found:

$$W^* = 2 \delta^2 k (1 - \varphi).$$

If we designate the coefficient of friction of the mixture with k^*, then:

$$W^* = 2 \delta^{*2} k^*.$$

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From the last three equations, omitting the infinitely small higher order, we get:

$$k^* = k(1 + \varphi).$$

Thus we get the result:

If very small rigid spheres are suspended in a liquid, the coefficient of internal friction increases by a fraction which is equal to the total volume of /301 the spheres suspended in the unit of volume, provided that this total volume is very small.

§ 3. The Volume of a Dissolved Substance of Large Molecular Volume in Comparison to the Solvent.

Let there be a dilute solution of a material which is undissociated in the solution. Let one molecule of the dissolved substance be larger than a molecule of the solvent and be assumed to be a rigid sphere of radius P. Then we can apply the result obtained in § 2. If k^* signifies the coefficient of friction of the solution, k signifies that of the tear solvent, so that:

$$\frac{k^*}{k} = 1 + \varphi,$$

in which φ is the total volume of the molecules found in the solution per unit of volume.

We wish to compute φ for a 1% aqueous sugar solution. According to the observations of Burkhard (Tables of Landolt and Bornstein) k^*/k = 1.0245 (at 20°C) in a 1% aqueous sugar solution, and thus φ = 0.0245 for (almost exactly) 0.01 grams of sugar. Thus 1 gram of sugar dissolved in water has the same influence on its coefficient of friction as small, suspended rigid spheres of a total volume of 2.45 cm^3.

It should now be recalled that 1 g of solid sugar possesses a volume of 0.61 cm^3. The same volume is also found for the specific volume s of the sugar found in solution, if we assume the sugar solution to be a *mixture* of water and sugar in a dissolved form. The density of a 1% aqueous sugar solution (referred to water of the same temperature) at 17.5° is actually 1.00388. Thus (disregarding the difference in density of water at 4° and water at 17.5°), we get:

$$\frac{1}{1,00388} = 0,99 + 0,01\,s;$$

thus

$$s = 0,61.$$

Thus, while the sugar solution in respect to its density behaves like a mixture of water and solid sugar, its influence on the internal friction is

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four times greater than would result from merely suspending the same amount of
sugar. It seems to me that this result, in the sense of molecular theory, can
hardly be explained except by assuming that a sugar molecule in solution regards
the mobility of the immediately adjacent water so that a quantity of water, of
which the volume is about three times the volume of the sugar molecule, is
chained to the sugar molecule.

We may thus say that a dissolved sugar molecule (or the molecule along
with the water held fast by it) behaves in a hydrodynamic relationship like a
sphere of volume 2.45 • $342/N$cm^3, where 342 is the molecular weight of the
sugar and N the number of actual molecules in 1 g molecule.

§ 4. The Diffusion of an Undissociated Material in a Fluid Solution.

Let there be a solution like the one considered in § 3. If a power K
effects the molecule, which we consider as a sphere of radius P, the molecule
moves with a velocity ω which is determined by P and the coefficient of equa-
tion k of the solvent. This is equation (22) of Kirchhoff's work [1]:

$$\omega = \frac{K}{6\pi k P}. \tag{1}$$

We shall use this equation to compute the coefficient of diffusion of an
undissociated solution. If p signifies the osmotic pressure of the dissolved
substance, which may be regarded as the only exciting power in the dilute
solution under consideration, the power exercised on the dissolved substance
per unit of volume of the solution in the direction of the X-axis is $-\partial p/\partial x$.
If ρ grams are found in a unit of volume and if m is the molecular weight of
the dissolved material, N the number of actual molecules in a gram molecule,
$(\rho/m)N$ is the number of (actual) molecules in the unit of volume and the power
exercised on one molecule as a result of the concentration gradient is:

$$K = -\frac{m}{\varrho N}\frac{\partial p}{\partial x}. \tag{2}$$

If the solution is diluted enough, the osmotic pressure is given by the
equation:

$$p = \frac{R}{m}\varrho T, \tag{3}$$

where T is the absolute temperature and $R = 8.31 • 10^7$. From equations (1), (2)
and (3), for the velocity of migration of the dissolved substance, we get:

$$\omega = -\frac{RT}{6\pi k\cdot NP}\frac{1}{\varrho}\frac{1}{\varrho}\frac{\partial\varrho}{\partial x}.$$

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Finally, the amount of material going through in the direction of the X-axis per unit of time through one unit of cross-section is :

$$\omega \varrho = - \frac{R\,T}{6\,\pi\,k} \cdot \frac{1}{N\,P} \frac{\partial\,\varrho}{\partial x}. \tag{4}$$

Thus for the coefficient of diffusion D we get

$$D = \frac{R\,T}{6\,\pi\,k} \cdot \frac{1}{N\,P}\,,$$

Thus it is possible to compute the product of the number N of actual molecules in a gram molecule and the hydrodynamically active molecular radius P from the coefficient of diffusion and the coefficient of the internal friction of the solvent.

In this derivation the osmotic pressure has been considered as a power working on the individual molecules, which obviously does not correspond to the concept of the kinetic molecular theory, since according to the latter, the osmotic pressure in the present case is only to be understood as an apparent power. However, this difficulty disappears if we reflect on the fact that the (dynamic) equilibrium can be provided for the (apparent) osmotic powers, which correspond to the concentration differences of the solution, by the powers operating on the individual molecules and both numerically equal and directed   /304 opposite to them, as can be easily understood in a thermodynamic manner.

The equilibrium can be provided for the osmotic power

$$- \frac{1}{\varrho} \frac{\partial\,p}{\partial x}$$

working on a unit of mass by the power $-P_x$ (dealing only with the individually dissolved molecules), if

$$- \frac{1}{\varrho} \frac{\partial\,p}{\partial x} - P_x = 0.$$

If we thus think of the dissolved substance (per unit of mass), dealing with the two mutually occurring power systems P_x and $-P_x$, $-P_x$ provides the equilibrium for the osmotic pressure, and only the power P_x numerically equal to the osmotic pressure is left as a cause of movement. In this way the difficulty mentioned is set aside[1].

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[1]An exhaustive presentation of this method of thought is found in Ann. d. Phys.,Vol. 17, p. 549, 1905.

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§ 5. Determining the Molecule Dimensions with the Help of the Acquired Relationships.

In § 3 we found:

$$\frac{k^*}{k} = 1 + \varphi = 1 + n \cdot \tfrac{4}{3}\pi P^3,$$

in which n signifies the number of dissolved molecules per unit of volume and P the hydrodynamically effective molecule radius. If we consider that

$$\frac{n}{N} = \frac{\varrho}{m},$$

in which ϱ signifies the mass per unit of volume of the dissolved material and m its molecular weight, we get:

$$N P^3 = \frac{3}{4\pi} \frac{m}{\varrho} \left(\frac{k^*}{k} - 1\right).$$

On the other hand we found in § 4:

$$N P = \frac{R T}{6\pi k} \frac{1}{D}.$$

Both of these equations enable us to compute the magnitudes P and N separately, of which N must be producible independently of the nature of the solvent, of /305 the dissolved substance and of the temperature, if our theory corresponds to the facts.

We wish to carry out the computation for an aqueous sugar solution. According to the data provided above on the internal friction of the sugar solution, it then follows for 20°C:

$$N P^3 = 200.$$

According to Graham's experiments (computed by Stefan), the coefficient of diffusion of sugar in water at 9.5°C is 0.384, if the day is chosen as a unit of time. The viscosity of water at 9.5° is 0.0135. We wish to introduce these data into our formula for the coefficient of diffusion; in spite of the fact that they were obtained for 10% solutions and exact validity is not to be expected of our formula at such high concentrations. We get

$$N P = 2.08 \cdot 10^{16}.$$

From the values found for $N P^3$ and $N P$, if we overlook the difference of

P at 9.5^0 and 20^0, it follows that

$$P = 9.9 \cdot 10^{-8} \text{ cm},$$

$$N = 2.1 \cdot 10^{23}.$$

The value found for N is in satisfactory agreement with the order of magnitude according to values found by other methods for this magnitude.

Bern, 30 August, 1905.

(Arrived 19 August 1905)

REFERENCES

1. Kirchhoff, *Vorlesungen uber Mechanik*, [Lecture on Mechanics]. Lecture 26.

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ADDENDUM

In the new addition of the physico-chemical tables of Landolt and Bornstein far more useful data are found for computing the magnitude of the sugar molecule and the number N of the actual molecule in a gram molecule.

For the coefficient of diffusion of sugar in water at 18.5°C and a concentration of 0.005 mol/liter, Thovert found (Table, p. 372) the value 0.33 cm²/ per day. From a table of results observed by Hosking (Table, p. 81) it is further found by interpolation that in diluted sugar solutions an increase in the coefficient of viscosity of 0.00025 corresponds to an increase in sugar content of 1% at 18.5°C.

On the basis of these data we find

$$P = 0.78 \cdot 10^{-6} \text{ mm}$$

and

$$N = 4.15 \cdot 10^{23}.$$

Bern, January 1906.